

CRUDE OIL DESULFURIZATION

FIELD OF THE INVENTION

5 The present invention is directed to a method for hydrodesulfurizing
6 crude oil.

BACKGROUND OF THE INVENTION

10 Crude oil is conventionally processed by distillation followed by various
11 cracking, solvent refining and hydroconversion processes to produce a
12 desired slate of fuels, lubricating oil products, chemicals, chemical feedstocks
13 and the like. An example conventional process includes distillation of a crude
14 oil in an atmospheric distillation column to form a gas oil, naphtha, a gaseous
15 product, and a atmospheric residuum. Generally, the atmospheric residuum
16 is further fractionated in a vacuum distillation column to produce a vacuum
17 gas oil and a vacuum residuum. The vacuum gas oil is usually cracked to
18 more valuable light transportation fuel products by fluid catalytic cracking or
19 hydrocracking. The vacuum residuum may be further treated to recover a
20 higher amount of useful products. Such upgrading methods may include one
21 or more of, for example, residuum hydrotreating, residuum fluid catalytic
22 cracking, coking, and solvent deasphalting. Streams recovered from crude
23 distillation at the boiling point of fuels have characteristically been used
24 directly as fuels.

25
26 U.S. Patent No. 4,885,080 teaches preparing a synthetic crude oil by
27 fractionating a heavy crude oil, hydrodesulfurizing the distillate cut,
28 hydrodemetallizing the residuum and combining the hydrotreated cuts with a
29 third liquid fraction to form the synthetic crude oil. U.S. Patent No. 3,830,731
30 teaches distilling a heavy hydrocarbon feedstock into a vacuum gas oil and a
31 vacuum residuum fraction, and hydrodesulfurizing each fraction.

1 However, increasingly tighter regulations on contaminant in fuels, particularly
2 sulfur and aromatics, have forced many refiners to hydrorefine most and often
3 all, of the fuel products. To meet the more stringent requirements for low
4 sulfur diesel, refiners have added naphtha hydrotreaters for removing sulfur
5 and nitrogen compounds from at least some of the refinery streams which go
6 to make up the gasoline pool. In response to the more stringent requirements
7 for clean diesel fuels, refiners have added diesel hydrotreaters for making the
8 low sulfur, low aromatics diesel which are now preferred, and often required.
9 More refiners are building hydrocrackers due to their ability to produce high
10 quality low sulfur fuels. The light gaseous products processed in a refinery
11 are generally treated to remove H₂S and others sulfur containing components
12 prior to use of the gaseous products for energy, as petrochemical feedstocks,
13 as reforming feedstocks for making synthesis gas, or as building blocks for
14 turning the gaseous products into higher molecular weight products.

15
16 Thus, in response to these tightening regulations, refiners have constructed
17 separate hydroprocessing units to upgrade each of the fuel streams produced
18 in the refinery. The net effect is a large number of similar processing units,
19 each handling a separate stream, requiring additional tankage and operators.
20 Specific streams are alternatively heated for reaction or fractionation, and
21 then cooled for separation and storage. Multiple reaction systems requires
22 multiple hydrogen supply, pressurization and distribution systems. It is
23 desirable to have a process for hydroprocessing the entire crude oil into
24 useful low aromatic, low sulfur products while significantly reducing the
25 number of refinery processing steps and processing equipment required to
26 convert the crude to useful products. Such a process is the subject of the
27 present invention.

28
29 In U.S. Patent No. 5,009,768, a complete crude or the atmospheric and
30 vacuum residues thereof mixed with vacuum gas oils is demetallized and the
31 demetallized product hydrotreated for hydrodenitrogenation and
32 hydroconversion. In U.S. Patent No. 5,382,349, a heavy hydrocarbon oil is
33 hydrotreated, the hydrotreated oil distilled and a vacuum residue thermally
34 hydrocracked in a slurry bed. U.S. Patent No. 5,851,381 provides a method

1 of refining crude oil by distillation and desulfurization. In the method, a
2 naphtha fraction is separated from crude oil by distillation, with the remaining
3 residual fraction after the naphtha fraction has been removed from the crude
4 oil being hydrodesulfurized and the hydrodesulfurized fraction separated into
5 further fractions, first in a high pressure separator and then by atmospheric
6 distillation. A residue is further upgraded in a residue fluid catalytic cracking
7 process.

8

9 SUMMARY OF THE INVENTION

10

11 In the present process, a crude oil feed is desulfurized and processed
12 (hydrotreated and hydrocracked) to form low sulfur, low aromatic fuels in an
13 integrated unit, with a single hydrogen supply and recovery loop, with minimal
14 cooling of intermediate products, and without tank storage of intermediate
15 products. The integrated unit comprises a series of catalytic reaction zones,
16 each containing a single catalyst or a layered catalyst system selected for a
17 particular application, whether it be desulfurization of a crude feed,
18 hydrocracking a gas oil stream or hydrotreating a particular stream to reduce
19 the aromatic and/or sulfur content of the stream to low levels. Flash
20 separation of reaction products exiting a particular catalytic reaction zone is
21 tailored to isolate hydrogen with minimal heat exchange beyond that required
22 to prepare the reaction products for the next processing step.

23

24 In the present invention, a crude oil feed is passed directly to a crude
25 desulfurization unit for desulfurization. The crude oil feed may be desalted
26 and volatile materials removed prior to desulfurization, but a substantial
27 portion of the crude oil feed is subjected to desulfurization in a desulfurization
28 reaction zone. A number of reactions is expected to occur during the
29 desulfurization process. Portions of the crude oil feed which contain
30 metal-containing components will be at least partially demetallized during the
31 desulfurization process. Likewise, nitrogen and oxygen are removed, along
32 with sulfur, during the desulfurization process. While the amount of cracked
33 products produced during desulfurization will be relatively small, some amount

1 of larger molecules will be cracked to lower molecular weight products during
2 the desulfurization process.

3
4 The desulfurized crude oil temperature is adjusted for fractionation, and a gas
5 oil fraction isolated. The gas oil fraction is available for use directly as a fuel.
6 Preferably, the gas oil fraction is further hydrotreated for additional sulfur,
7 nitrogen and/or aromatic removal. Yields of desirable fuel products are
8 increased in the present process when the desulfurized crude oil product is
9 fractionated, preferably in a multi-stage fractionation zone having atmospheric
10 and vacuum distillation columns. Products from multi-stage distillation include
11 a light gas oil fraction, a vacuum gas oil fraction and a residual fraction. The
12 light gas oil fraction, generally having a normal boiling of less than 700°F, may
13 be used directly as a fuel, or further hydroconverted for improved fuel
14 properties. The vacuum gas oil fraction is hydrocracked to increase the fuel
15 yield in the present process and to further improve fuel properties. Single or
16 multi-stage hydrocracking reactors may be employed. The hydrocracked
17 products includes at least one low sulfur fuel product, which may be isolated
18 from a step of distilling the hydrocracked products.

19
20 Accordingly, a process is provided for hydrodesulfurizing a crude oil feed in a
21 crude desulfurization unit, separating the desulfurized crude oil and isolating a
22 light gas oil fraction, a vacuum gas oil fraction and a residual fraction,
23 hydrocracking the vacuum gas oil to form at least one low sulfur fuel product;
24 and hydrotreating the light gas oil fraction. This entire integrated process may
25 be conducted without using tank storage of intermediate products, such as a
26 desulfurized crude oil, a light gas oil fraction, and a vacuum gas oil fraction.
27 Further, with no required tank storage of intermediate products, the preferred
28 process can be conducted without cooling of the intermediate products, thus
29 reducing the operating cost of the process. In a further cost savings, the
30 hydroconversion steps of the present process, including crude desulfurization,
31 hydrocracking and hydrotreating, are suitably conducted using a single
32 hydrogen supply loop, thus further reducing the capital and operating cost of
33 the process.

1 The present invention provides an integrated refining system for processing a
2 whole crude, or a substantial portion of a whole crude, into a full range of
3 product materials at high selectivities and high yields of the desired products.
4 The integrated process of the present invention further provides a series of
5 reaction zones, containing catalysts of varying pore volume, for successively
6 converting progressively lighter and cleaner products in the production of fuel
7 products. The integrated process further provides a method for isolating,
8 purifying and providing hydrogen to the various conversion reaction zones
9 through the use of a single hydrogen isolation and pressurization unit. Among
10 other factors, the present invention is based on an improved understanding of
11 hydroconversion processes, permitting more efficient use of a combination of
12 units for reaction, for product isolation, for hydrogen isolation and recycle, and
13 for energy usage in the preparation of fuels from a crude feed. In the process,
14 a wide range of fuel oil products can be safely prepared with a small number
15 of reaction vessels and product recovery vessels, and with a minimum
16 number of supporting vessels, for handling hydrogen and intermediate
17 products, and employing a minimum number of operators. In effect, the
18 present invention is based on the novel combination of crude desulfurization
19 tailored to a wide boiling range feed, followed by distillation to form a few
20 distillate streams, and bulk upgrading in an integrated
21 hydrocracking/hydrotreating process to form a wide range of useful fuel and
22 lubricating oil base stock products. The present process provides an efficient
23 and less costly alternative to the conventional refinery practice of separating a
24 crude oil feed into a number of distillate and residuum fractions, each of which
25 are processed individually in similar but separate upgrading processes.

DESCRIPTION OF THE FIGURES

3 Figure 1 discloses a crude oil desulfurization process which comprises the
4 following steps:

- 5 a) hydrodesulfurizing a crude oil feed in a crude desulfurization unit;
- 6 b) separating the desulfurized crude oil and recovering a light gas oil
- 7 fraction, a vacuum gas oil fraction and a vacuum residuum fraction;
- 8 c) hydrocracking the vacuum gas oil to form at least one low sulfur fuel
- 9 product; and
- 10 d) hydrotreating the light gas oil fraction.

12 Figure 2 discloses a crude oil desulfurization process which comprises the
13 following steps:

- 14 a) hydrodesulfurizing a crude oil feed;
- 15 b) separating the desulfurized crude oil and recovering at least a light
- 16 gas oil fraction, a vacuum gas oil fraction and a residual fraction;
- 17 c) hydrocracking the vacuum gas oil in a first hydrocracking reaction
- 18 zone to reduce the sulfur content and the nitrogen content therefrom
- 19 and to produce a low sulfur gas oil product;
- 20 d) hydrocracking the low sulfur gas oil product in a second
- 21 hydrocracking reaction zone at a conversion of at least 20% to form
- 22 at least one low sulfur fuel product; and
- 23 e) hydrotreating the light gas oil fraction.

1 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

2 DEFINITIONS

3

4 For the purposes of this specification, the term "middle distillates" as used
5 herein is to be taken as a reference to hydrocarbons or hydrocarbon mixtures
6 having a boiling point or boiling point range substantially corresponding to that
7 of the kerosene and diesel fractions obtained during the conventional
8 atmospheric distillation of crude oil feed. The term "light gas oil" (LGO) as
9 used herein is to be taken as a reference to hydrocarbons or hydrocarbon
10 mixtures which are isolated as distillate streams obtained during the
11 conventional atmospheric distillation of a refinery stream, a petroleum stream
12 or a crude oil stream. The term "vacuum gas oil" (VGO) as used herein is to
13 be taken as a reference to hydrocarbons or hydrocarbon mixtures which are
14 isolated as distillate streams obtained during the conventional vacuum
15 distillation of a refinery stream, a petroleum stream or a crude oil stream. The
16 term "naphtha" as used herein is a reference to hydrocarbons or hydrocarbon
17 mixtures having a boiling point or boiling point range substantially
18 corresponding to that of the naphtha (sometimes referred to as the gasoline)
19 fractions obtained during the conventional atmospheric distillation of crude oil
20 feed. In such a distillation, the following fractions are isolated from the crude
21 oil feed: one or more naphtha fractions boiling in the range of from 30 to
22 220°C, one or more kerosene fractions boiling in the range of from 120 to
23 300°C and one or more diesel fractions boiling in the range of from 170 to
24 370°C. The boiling point ranges of the various product fractions isolated in
25 any particular refinery will vary with such factors as the characteristics of the
26 crude oil source, refinery local markets, product prices, etc. Reference is
27 made to ASTM standards D-975 and D-3699-83 for further details on
28 kerosene and diesel fuel properties. The term "hydrocarbon fuel" is to be
29 taken as a reference to either one or a mixture of naphtha and middle
30 distillates. Unless otherwise specified, all distillation temperatures listed
31 herein refer to normal boiling point and normal boiling range temperatures.
32 By "normal" is meant a boiling point or boiling range based on a distillation at
33 one atmosphere pressure, such as that determined in a D1160 distillation.

1 The term "hydrotreating" as used herein refers to a catalyst process wherein a
2 suitable hydrocarbon-based feed stream is contacted with a hydrogen-
3 containing treat gas in the presence of suitable catalysts for removing
4 heteroatoms, such as sulfur and nitrogen and for some hydrogenation of
5 aromatics.

6

7 The term "desulfurization" as used herein refers to a catalyst process wherein
8 a suitable hydrocarbon-based feed stream is contacted with a
9 hydrogen-containing treat gas in the presence of suitable catalysts for
10 removing heteroatoms such as sulfur atoms from the feed stream.

11

12 The term "hydrocracking" as used herein refers to a catalyst process wherein
13 a suitable hydrocarbon-based feed stream is contacted with a hydrogen-
14 containing treat gas in the presence of suitable catalysts for reducing the
15 boiling point and the average molecular weight of the feed stream.

16

17 CRUDE DESULFURIZATION UNIT

18

19 The crude oil feed to the present process is generally a whole crude which
20 has not been substantially separated into individual fractions. Removing
21 volatile gases and light liquids (including C₁ to C₄ hydrocarbons) prior to
22 introducing the crude oil feed to the crude desulfurization unit is generally
23 preferred. The crude oil feed is also treated in a desalting unit prior to
24 desulfurization. The full benefits of the practice of the invention are equally
25 realized if a naphtha fraction is removed from the crude oil feed prior to
26 treating in the crude desulfurization unit.

FIGURE 1 REACTOR CONFIGURATION

4 Referring now to Fig. 1, a crude oil feed **02** is passed to a crude
5 desulfurization unit **04** in combination with a hydrogen rich stream **44** for
6 hydrodesulfurizing the crude oil feed. Crude desulfurization unit **04** comprises
7 one or more reaction zones, each of which contains one or more catalyst
8 beds. The crude desulfurization unit removes a substantial portion of the
9 contaminants present in the crude oil feed, including metals, sulfur, nitrogen
10 and Conradson carbon. Catalysts provided in crude desulfurization unit **04** for
11 removing these contaminants may include a single catalyst or a layered
12 catalyst system comprising multiple catalysts present in one or more reactors.
13 When using a reaction train comprising more than one reactor in series
14 operation, a major portion, if not all, of the liquid product from each reactor
15 (except the last reactor vessel in the reaction train) is passed to a next reactor
16 for additional processing. In the layered catalyst system, catalysts are pre-
17 selected for their intended specific use, whether it be demetallation, or sulfur
18 and nitrogen removal, or asphaltene and Conradson carbon removal, or mild
19 conversion. Different catalyst layers may also be selected to facilitate the
20 desulfurization of various boiling point fractions present in the crude oil feed,
21 including naphtha fractions, middle distillate fractions, vacuum gas oil
22 fractions and/or residuum fractions.

DESULFURIZATION UNIT CATALYST

26 Catalysts for use in the crude desulfurization unit **04** are generally composed
27 of a hydrogenation component, selected from Group VIb (preferably
28 molybdenum and/or tungsten, more preferably molybdenum) and Group VIII
29 (preferably cobalt and/or nickel) of the Periodic Table, or a mixture thereof, all
30 supported on an alumina support. Phosphorous (Group Va) oxide is
31 optionally present as an active ingredient. A typical desulfurization catalyst
32 contains from 3 to 35 wt% hydrogenation components, with an alumina
33 binder.

1 The catalyst pellets range in size from 1/32 inch to 1/8 inch. A spherical,
2 extruded, trilobate or quadrilobate shape is preferred. In general, the crude oil
3 feed passing through the desulfurization unit contacts first a catalyst
4 preselected for metals removal, though some sulfur, nitrogen and aromatic
5 removal will also occur. Subsequent catalyst layers are preselected for sulfur
6 and nitrogen removal, though they would also be expected to catalyze the
7 removal of metals and/or cracking reactions.

8

9 Catalyst layer(s) preselected for demetallization comprise catalyst(s) having
10 an average pore size ranging from 125 to 225 Å and a pore volume ranging
11 from 0.5 - 1.1 cm³/g. Catalyst layer(s) preselected for
12 denitrification/desulfurization comprise catalyst(s) having an average pore
13 size ranging from 100 to 190 Å with a pore volume of 0.5 - 1.1 cm³/g.
14 U.S. Patent No. 4,90,243 describes a hydrotreating catalyst having a pore
15 size of at least about 60 Å, and preferably from about 75 Å to about 120 Å. A
16 demetallation catalyst useful for the present process is described, for
17 example, in U.S. Patent No. 4,976,848, the entire disclosure of which is
18 incorporated herein by reference for all purposes. Likewise, catalysts useful
19 for desulfurization of heavy streams are described, for example, in
20 U.S. Patent No. 5,215,955 and U.S. Patent No. 5,177,047, the entire
21 disclosures of which is incorporated herein by reference for all purposes.
22 Catalysts useful for desulfurization of middle distillate, vacuum gas oil streams
23 and naphtha streams are described, for example, in U.S. Patent
24 No. 4,990,243 the entire disclosures of which are incorporated herein by
25 reference for all purposes.

26

27 REACTION CONDITIONS

28

29 It is desirable that the crude desulfurization unit **04** be controlled to maintain
30 the product sulfur at a specified maximum concentration. For example, when
31 the product sulfur is maintained at less than 1 wt% based on feed, and
32 preferably less than 0.75 wt% based on feed, reaction conditions in the crude
33 desulfurization unit **04** include a reaction temperature between about 315°C
34 and 440°C (600°F – 825°F), pressures from 6.9 MPa to about 20.7 MPa

1 (1000 - 3000 psi), and a feed rate (vol oil/vol cat hr) from 0.1 to about 20 hr⁻¹.
2 Hydrogen circulation rate are general in the range from about 303 std liter
3 H₂/kg oil to 758 std liters H₂/kg oil (2000-5000) standard cubic feet per barrel).

4

5 DESULFURIZED CRUDE OIL PROPERTIES

6

7 The crude oil desulfurization process removes greater than 25% w/w,
8 preferably greater than 50% w/w of the sulfur present in the crude oil feed **02**.
9 The preferred desulfurized crude oil **06** typically has a sulfur content of less
10 than 1 wt%, preferably less than 0.75 wt%, still more preferably less than
11 0.5 wt%.

12 DESULFURIZED CRUDE DISTILLATION

13

14 Unreacted hydrogen isolated from crude desulfurization unit **04** is separated
15 from desulfurized crude oil **06** in one or more flash zones **08** (e.g. a
16 desulfurization unit high pressure separator) and the resultant desulfurized
17 liquid **10** is passed to crude fractionator **12** for fractionation to produce at least
18 a light gas oil fraction **20**, a vacuum gas oil fraction **18** and a residuum
19 fraction **16**. Crude fractionator **12** is a single or multiple column fractionation
20 system, and preferably a two column or stage fractionator. One example two-
21 stage fractionator comprises an atmospheric distillation column operated
22 substantially at or slightly above atmospheric pressure, and a vacuum
23 distillation column operated at sub-atmospheric pressure. Such distillation
24 column systems are well known. In a preferred process of the invention,
25 desulfurized liquid **10** is passed from flash separation zone(s) **08** directly to
26 crude fractionator **12** without cooling desulfurized liquid **10** beyond that
27 required for the distillation in crude fractionator **12**. The temperature of at
28 stream **10** passing from **8** to **12** is preferably maintained at a temperature of at
29 least 250°F, and preferably of at least 600°F. In the embodiment illustrated in
30 Fig. 1, all of the desulfurized crude oil, absent light gases, are passed to crude
31 fractionator **12** for fractionation.

HYDROCRACKING UNIT

3 The vacuum gas oil fraction **18** from the crude fractionator **12** is passed to the
4 hydrocracking unit **54**, preferably directly, without tankage and with minimal
5 heat removal, for further processing to produce low sulfur and low aromatic
6 hydrocarbon fuels. The hydrocracking unit **54** contains catalyst selected for
7 further removal of sulfur and nitrogen compounds, for saturation and removal
8 of aromatic compounds, and for cracking for molecular weight reduction. For
9 the present invention, conversion is generally related to a reference
10 temperature, such as, for example, the minimum boiling point temperature of
11 the hydrocracker feedstock. The extent of conversion relates to the
12 percentage of feed boiling above the reference temperature which is
13 converted during hydrocracking into hydrocrackate boiling below the
14 reference temperature. Where the reference temperature is selected to be,
15 e.g. 370°C (700°F), overall conversion during hydrocracking in hydrocracking
16 unit **54** is typically greater than 10%, and preferably greater than 20%.

2ND STAGE PRODUCT

20 Effluent from hydrocracking unit **54** is separated in one or more flash
21 separation units **28** (e.g. hydrocracker separation unit) to isolate at least a
22 hydrocracked liquid product **62**, which is passed to product fractionator **30** for
23 fractionation. In the preferred process, recycle H₂ stream **56** is separated
24 from hydrocracked effluent **52** for recycle to various units in the integrated
25 process, and the remaining liquid **62** is passed to a product fractionator **30** for
26 isolating fuel product(s). The purity of recycle H₂ stream **56** will generally be
27 maintained at greater than 75 mole% hydrogen. In order to maintain energy
28 efficiency, hydrocracked liquid product **62** is passed to fractionator **30** without
29 substantial cooling of **62**. At least one fuel product, **40**, is isolated from
30 product fractionator **30**.

NAPHTHA PRODUCT

3 Light gas oil **20** is isolated from crude fractionator **12**. This stream may be
4 blended into a gasoline pool without further processing if desired, particularly
5 if the sulfur level of light gas oil **20** is below 300 ppm, and preferably below
6 100 ppm. Alternatively, light gas oil **20** is hydrotreated in hydrotreating
7 reaction zone **58** to reduce sulfur levels to below 100 ppm, preferably below
8 50 ppm, and more preferably below 15 ppm. Stream **60** is isolated as
9 desirably low sulfur naphtha.

FIGURE 2

CRUDE OIL DESULFURIZATION

13 In the preferred embodiment illustrated in Fig. 2, crude oil feed **02** is passed to
14 crude desulfurization unit **04** for removing contaminants, e.g. one or more of
15 sulfur, nitrogen, asphaltenes, Conradson carbon, from the crude oil feed **02**.
16 As described above with respect to Fig. 1, desulfurized crude oil **06** is treated
17 in one or more flash zones **08** to remove unreacted hydrogen and light
18 hydrocarbon products **14**. The desulfurized liquid **10** from the flash zone(s)
19 **08** is then passed to a crude fractionator **12**. In a preferred process of the
20 invention, desulfurized liquid **10** is passed from flash separation zone(s) **08**
21 directly to crude fractionator **12** without cooling desulfurized liquid **10** beyond
22 that required for the distillation in crude fractionator **12**. The temperature of
23 stream **10** passing from **8** to **12** is preferably maintained at a temperature of at
24 least 250°F, and preferably of at least 300°F. At least residuum fraction **16**,
25 vacuum gas oil **18**, and light gas oil **20** are isolated from crude fractionator **12**.

DESULFURIZED PRODUCT DISTILLATION

29 Fractionation zone **12** may be a single distillation column, or multiple
30 distillation columns, each positioned in serial flow with respect to the other. In
31 a preferred embodiment of the process, the desulfurized liquid **10** is
32 fractionated in fractionation zone **12** which comprises at least one distillation
33 column (not shown) which is operated substantially at or slightly above
34 atmospheric pressure (i.e. an atmospheric distillation column) and at least one

1 distillation column (not shown) which is operated at sub-atmospheric pressure
2 (i.e. a vacuum distillation column). Such distillation columns are well known in
3 the art. Desulfurized liquid **10** is passed to the atmospheric distillation column
4 to produce at least naphtha stream **20** and an atmospheric residuum, which is
5 further fractionated in the vacuum distillation column. A vacuum gas oil **18** is
6 isolated as a distillate fraction from the vacuum distillation column, and
7 vacuum residuum stream **16** is isolated as a bottoms fraction from the
8 vacuum distillation column.

9
10 The vacuum gas oil **18** is passed directly to hydrocracker unit hydrocracking
11 unit **54** for conversion to lower molecular weight products and for reduction in
12 sulfur, nitrogen and/or aromatic content. As shown in the preferred
13 embodiment illustrated in Fig. 2, the hydroconversion step involves at least
14 two reaction vessels, first hydrocracker stage **22** and second hydrocracker
15 stage **26**. The hydrocracking process is especially useful in the production of
16 middle distillate fractions boiling in the range of about 250°-700° F.
17 (121°-371° C.) as determined by the appropriate ASTM test procedure. The
18 hydrocracking process involves conversion of a petroleum feedstock by, for
19 example, molecular weight reduction via cracking, hydrogenation of olefins
20 and aromatics, and removal of nitrogen, sulfur and other heteroatoms. The
21 process may be controlled to a certain cracking conversion or to a desired
22 product sulfur level or nitrogen level or both. Conversion is generally related
23 to a reference temperature, such as, for example, the minimum boiling point
24 temperature of the hydrocracker feedstock. The extent of conversion relates
25 to the percentage of feed boiling above the reference temperature which is
26 converted during hydrocracking into hydrocrackate boiling below the
27 reference temperature.

HYDROGEN RECOVERY

3 The hydrogen stream **14** isolated from flash separation zone **08** may be
4 further purified in, for example, an amine scrubber **46** to remove some or all of
5 the H₂S and NH₃ gases. Following compression, the purified hydrogen is
6 passed to the first hydrocracker stage **22** and the second hydrocracker stage
7 **26**.

1ST STAGE

10 Reaction in first hydrocracker stage **22** is maintained at conditions sufficient to
11 further remove nitrogen and sulfur contaminants from the vacuum gas oil feed
12 **18** and for reducing the aromatic content of the vacuum gas oil feed **18**.
13 These hydrotreating reactions are generally characterized by a low amount of
14 conversion, e.g. less than 20%, preferably less than 15%. In general, it is
15 desirable to lower the nitrogen content of the hydrocarbon feedstock stream to
16 less than 50 parts per million by weight (ppm), preferably less than about 10
17 ppm and for increased catalyst life to a level of less than 2 ppm or even as
18 low as about 0.1 ppm. Similarly, it is generally desirable to lower the sulfur
19 content of the hydrocarbon feedstock stream to less than about 0.5% by
20 weight percent, preferably less than about 0.1%, and in many cases as low as
21 about 1 ppm.

1ST STAGE CONDITIONS

25 Thus, the one or more reaction zones in first hydrocracker stage **22** are
26 operated at reaction temperatures between 250°C and about 500°C
27 (482 - 932°F), pressures from 3.5 MPa to about 34.2 MPa (500 - 3500 psi) ,
28 and a feed rate (vol. oil/vol. cat h) from 0.1 to about 20hr⁻¹ . Hydrogen
29 circulation rates are in general in the range from about 350-std. liter H₂/kg oil
30 to 1780 H₂/kg oil (2310 - 11750 standard cubic feet per barrel). Preferred
31 reaction temperatures range from 340°C to about 455°C (644 - 851°F).
32 Preferred total reaction pressures range from 7.0 MPa to about 20.7 MPa
33 (1000 - 3000 psi).

1ST STAGE CATALYST

3 Catalysts useful in first hydrocracker stage **22** generally contain at least one
4 Group VIb metal (e.g. molybdenum) and at least one Group VIII metal
5 (e.g. nickel or cobalt) on an alumina support. A phosphorous oxide
6 component and a cracking component, such as silica-alumina and/or a
7 zeolite, may also be present. A layered catalyst system may also be used,
8 e.g. the layered catalyst system taught in U.S. Patent No. 4,990,243, which is
9 incorporated herein by reference for all purposes. The catalyst selected for
10 use in first hydrocracker stage **22** will generally have a pore volume in the
11 range of 0.5 to 1.2 cm³/g, with an average pore diameter of between 100 Å
12 and 180 Å, and a surface area 120 and 400 m²/g, wherein at least 60% of the
13 pores have a pore diameter of more than 100 Å. The first stage catalyst could
14 also be a layered system of hydrotreating and hydrocracking catalysts. The
15 preferred catalyst for first hydrocracker stage **22** comprises a nickel
16 molybdenum or cobalt molybdenum hydrogenation component and a
17 silica-alumina component with an alumina binder.

HOT H2 STRIPPER

21 The effluent **48** from the first hydrocracking stage **22** contains unreacted
22 hydrogen, gaseous and liquid products. Hydrogen isolated from effluent **48**
23 contains H₂S and NH₃. In conventional processes, such hydrogen is purified
24 prior to use as recycle to the first hydrocracking stage or as H₂ feed to the
25 second hydrocracking stage. The present process is based on the realization
26 that hydrogen isolated from effluent **48** is suitable for use as H₂ feed to the
27 crude desulfurization unit **04**, without extensive purification. The use of
28 hydrogen in this way is facilitated by passing effluent **48** to hot hydrogen
29 stripper **24** for removing light gases contained therein, including hydrogen and
30 light hydrocarbon gases, using heated hydrogen **36**. Typically, hot hydrogen
31 stripper **24** is operated at temperatures preferably between 260°C and 399°C
32 (500°F and 750°F). Hydrogen-rich stream **44**, which is isolated from hot
33 hydrogen stripper **24**, is combined with crude oil feed **02**, preferably with no
34 further purification, for desulfurizing crude oil feed **02** in crude desulfurization

1 unit **04**. Stripped effluent **50** isolated from hot hydrogen stripper **24** is passed
2 to second hydrocracker stage **26** for further upgrading. In a preferred
3 embodiment of the process, effluent **48** passes directly from reaction zone **22**
4 to a single stage **24** for hot hydrogen stripping. Stripped effluent **48** is then
5 passed directly as a heated liquid, with no cooling beyond the normal minimal
6 cooling associated with movement through the pipes connecting the various
7 processing units, to second hydrocracker stage **26** for further reaction.

8

9 2ND STAGE

10

11 Second hydrocracker stage **26** is a hydrocracking stage, operated at
12 hydrocracking conditions and with a catalyst(s) suitable for molecular weight
13 reduction, with additional sulfur, nitrogen and aromatics removal. Conditions
14 in second hydrocracker stage **26** are suitable for per pass conversions of up
15 to 90%. Indeed, operating second hydrocracker stage **26** in extinction recycle
16 mode, with partially reacted product being recycled until all have been
17 cracked, is also within the scope of the present process.

18

19 2ND STAGE CONDITIONS

20

21 The hydrocracking conditions used in the hydrocracker will range from 250°C
22 to about 500°C (482 - 932°F), pressures from about 3.5 MPa to about
23 24.2 MPa (500 - 3500 psi), and a feed rate (vol. Oil/ vol. cat h) from 0.1 to
24 about 20 hr⁻¹. Hydrogen circulation rates are generally in the range from
25 about 350 std liters H₂/kg oil to 1780 std liters H₂/kg oil (2310 - 11750
26 standard cubic feet per barrel). Preferred total reaction pressures range from
27 7.0 MPa to about 20.7 MPa (1000 - 3000psi). Second hydrocracker stage **26**
28 is operated at temperatures of greater than 650°F and pressures between
29 about 1000 psig and 3500 psig, preferably between 1500 psig and 2500 psig
30 hydrogen pressure.

2ND STAGE CATALYST

3 The catalyst used in the second hydrocracking stage **26** is a conventional
4 hydrocracking catalyst of the type used to carry out hydroconversion reactions
5 to produce transportation fuels. First hydrocracker stage **22** and second
6 hydrocracker stage **26** can contain one or more catalyst in more than one
7 reaction zone. If more than one distinct catalyst is present in either or the
8 reaction zones, they may either be blended or be present as distinct layers.
9 Layered catalyst systems are taught, for example, in U.S. Patent
10 No. 4990243. Hydrocracking catalyst useful for second hydrocracker stage
11 **26** are well known. In general, the hydrocracking catalyst comprises a
12 cracking component and a hydrogenation component on an oxide support
13 material or binder. The cracking component may include an amorphous
14 cracking component and/or a zeolite, such as a y-type zeolite, and ultrastable
15 Y type zeolite, or a dealuminated zeolite. Particularly preferred catalytic
16 cracking catalysts are those containing at least one zeolite which is normally
17 mixed with a suitable matrix such as alumina, silica or silica-alumina. A
18 suitable amorphous cracking component is silica-alumina. The preferred
19 amorphous cracking component is between 10 and 90 weight percent silica,
20 preferably between 15 and 65 weight percent silica, the remainder being
21 alumina. A cracking component containing in the range from about 10% to
22 about 80% by weight of the Y-type zeolite and from about 90% to about 20%
23 by weight of the amorphous cracking component is preferred. Still more
24 preferred is a cracking component containing in the range from about 15% by
25 weight to about 50% by weight of the Y-type zeolite, the remainder being the
26 amorphous cracking component. Also, so-called x-ray amorphous zeolites
27 (i.e., zeolites having crystallite sizes too small to be detected by standard
28 x-ray techniques) can be suitably applied as cracking components.
29 Hydrogenation components suitable for the hydrocracking and/or
30 hydrotreating catalysts which are used in the present integrated process
31 include those which are comprised of at least one Group VIII
32 (IUPAC Notation) metal, preferably iron, cobalt and nickel, more preferably
33 cobalt and/or nickel and at least one Group VI (IUPAC Notation) metal,
34 preferably molybdenum and tungsten, on a high surface area support

1 material, preferably alumina. Other suitable catalysts include zeolitic
2 catalysts, as well as noble metal catalysts where the noble metal is selected
3 from palladium and platinum. It is within the scope of the present invention
4 that more than one type of catalyst be used in the same reaction vessel. The
5 Group VIII metal is typically present in an amount ranging from about 2 to
6 about 20 weight percent. The Group VI metal will typically be present in an
7 amount ranging from about 1 to about 25 weight percent. The hydrogenation
8 components in the catalyst may be in the oxidic and/or the sulfidic form. If a
9 combination of at least a Group VI and a Group VIII metal component is
10 present as (mixed) oxides, it will be subjected a sulfiding treatment prior to
11 proper use in hydrotreating or hydrocracking. Suitably, the catalyst comprises
12 one or more components of nickel and/or cobalt and one or more components
13 of molybdenum and/or tungsten or one or more components of platinum
14 and/or palladium. Catalysts containing nickel and molybdenum, nickel and
15 tungsten, platinum and/or palladium are particularly preferred.

16
17 The effective diameter of the zeolite catalyst particles are in the range of from
18 about 1/32 inch to about 1/4 inch, preferably from about 1/20 inch to about 1/8
19 inch. The catalyst particles may have any shape known to be useful for
20 catalytic materials, including spheres, cylinders, fluted cylinders, prills,
21 granules and the like. For non-spherical shapes, the effective diameter can
22 be taken as the diameter of a representative cross section of the catalyst
23 particles. The catalyst particles will further have a surface area in the range of
24 from about 50 to about 500 m²/g.

25

26 LAYERED HYDROCRACKING ZONE FOR LIGHT GAS OIL
27 HYDROTREATING

28

29 In Fig. 1, a light gas oil stream **20** isolated from the desulfurized liquid **10** is
30 hydrotreated in **58** to remove sulfur and/or aromatics in preparation of a low
31 sulfur, low aromatic fuel product **60**. In a separate preferred embodiment
32 illustrated in Fig. 2, the hydrotreating catalyst useful for hydrotreating light gas
33 oil stream **20** is layered at or near the bottom of second hydrocracker stage
34 **26**. Thus, second hydrocracker stage **26** includes a layered catalyst system,

1 with catalysts typically used for hydrocracking near the feed inlet to second
2 hydrocracker stage **26** and one or more layers of catalyst typically used for
3 hydrotreating near the product effluent outlet of second hydrocracker stage
4 **26**. The amount of hydrotreating catalyst in second hydrocracker stage **26** is
5 generally smaller than the amount of hydrocracking catalyst included in
6 second hydrocracker stage **26**. In including the hydrotreating catalyst as a
7 layer in an otherwise hydrocracking reaction mode, it is expected that the
8 effluent from the catalyst layers for hydrocracking, having reacted at
9 hydrocracking conditions in second hydrocracker stage **26**, would not be
10 modified to any significant extent in the layer of hydrotreating catalyst in
11 second hydrocracker stage **26**. However, the unreacted hydrogen in the
12 reacting stream passing from the bed(s) of hydrocracking catalyst are
13 available for further reaction without additional heating, pressurization and/or
14 purification. Thus, light gas oil stream **20** stream, which is essentially fuel
15 boiling range material, but with higher amounts of sulfur, nitrogen and/or
16 aromatics than is permitted for current fuels, is passed to the portion of
17 second hydrocracker stage **26** which contains the layer(s) of hydrotreating
18 catalyst. Bypassing the hydrocracking catalyst beds reduces the amount of
19 undesirable cracking of light gas oil **20** stream. Furthermore, reaction of light
20 gas oil stream **20** in combination with the effluent from the layers of
21 hydrocracking catalyst of second hydrocracker stage **26** serves to remove
22 additional contaminants from light gas oil stream **20** without molecular weight
23 reduction and without added hydrogen beyond that potentially required to
24 quench exothermic heat release from the layers of hydrotreating catalyst in
25 second hydrocracker stage **26**. The reaction conditions for hydrotreating the
26 naphtha stream in the second hydrocracker stage is expected to be the same
27 as reaction conditions for hydrocracking in that stage. The blend of fuels
28 produced in the various catalyst layers of second hydrocracker stage **26** is
29 separated in product fractionator **30**. At least one fuel stream, shown as **40** in
30 Fig. 2, is isolated from product fractionator **30**.

2ND STAGE PRODUCT

3 Effluent **52** from second hydrocracker stage **26** is separated in hydrocracker
4 flash separation zone(s) **28** to isolate at least a recycle hydrogen stream **42**
5 and a hydrocracked liquid product **62**, which is passed to product fractionator
6 **30** for fractionation. At least one low sulfur fuel product, **40**, is isolated from
7 product fractionator **30**. However, it is expected that a full range of fuel
8 products, including low sulfur naphtha, low sulfur kerosene and low sulfur
9 diesel would desirably be isolated in the process. Stream **56** is combined with
10 fresh hydrogen **32** and with isolated hydrogen stream **14** as hydrogen feed to
11 first hydrocracker stage **22**, to hot hydrogen stripper **24** to second
12 hydrocracker stage **26**. Incompletely reacted products from second
13 hydrocracker stage **26** are recycled via **42** to second hydrocracker stage **26**.